

Novel Tertiary Amine Solid Adsorbents Used for the Capture of Carbon Dioxide

McMahan L. Gray

Daniel Fauth

Kenneth Champagne

Eric Beckman

Thomas Tarka



Presentation Outline

- Overview and Background
- Preliminary System Analysis
- Experimental Conditions and Results
- Conclusions



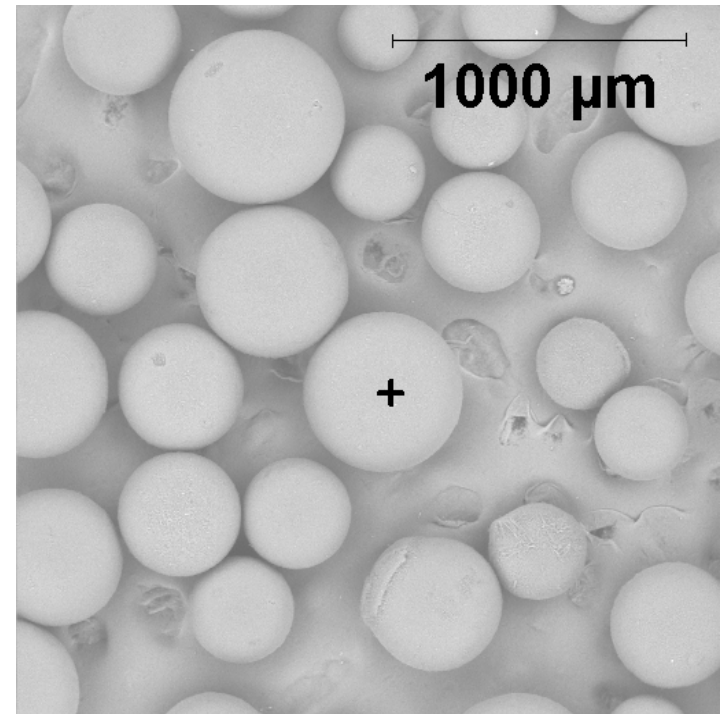
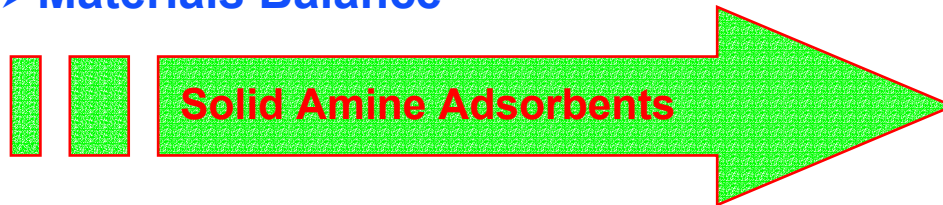
Overview and Background



Background – Carbon Dioxide Capture Technologies

Technical Challenges for Liquid Amine System

- Capture Capacities
- Energy Requires
- Mass and Heat Thermodynamics
- Amine Degradation
- Waste Products
- Corrosion Inhibitors
- Materials Balance

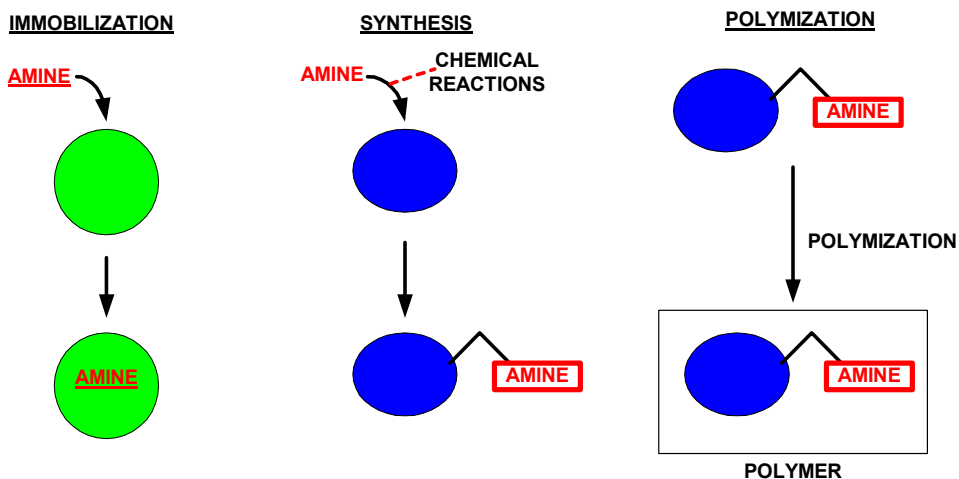


To develop low-cost solid adsorbents to be used in an efficient process for the capture of CO₂ from flue gas streams



Background - Adsorbent Parameters

Adsorbent Pathways



Adsorbent Criteria

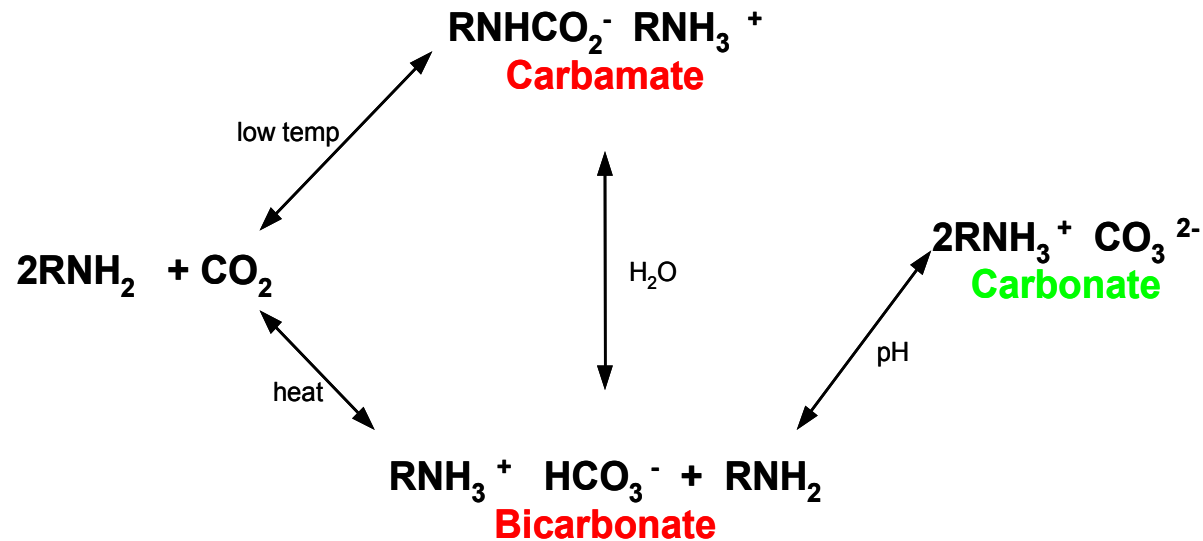
- Basicity
- Vapor Pressure
- Viscosity
- Substrate
- Capture Capacity
- Temperature Stability
- Regenerable
- Durability
- Flue Gas Stream

Performance and Cost



Overview and Background

Proposed Reaction Sequence (in solution)

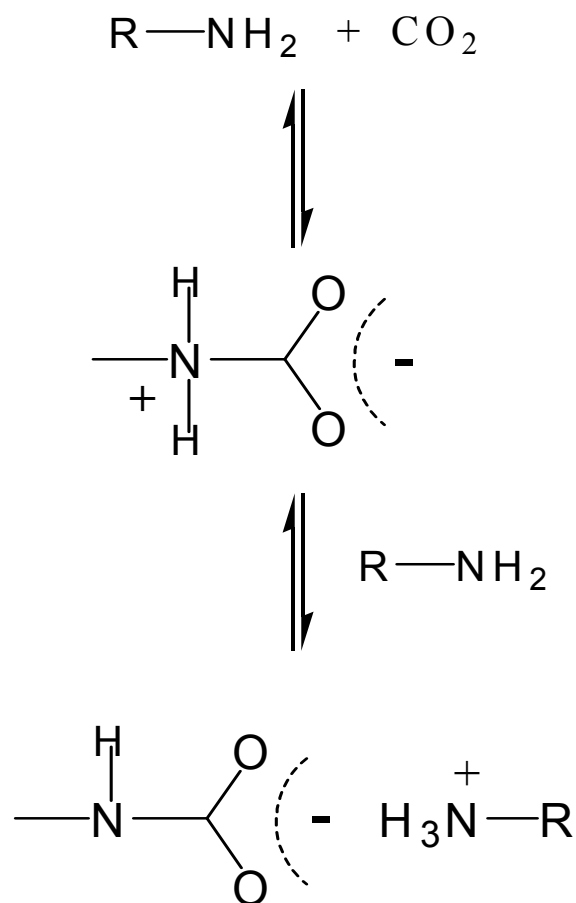


Hook, R. J., *Ind. Eng. Chem. Res.*, **1997**, 36, 1779 -1790



Overview and Background

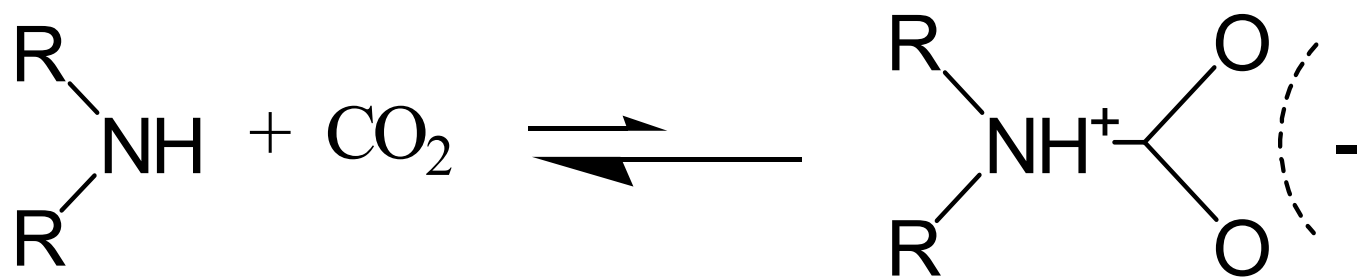
Brief Background on Amine-CO₂ Chemistry



Conventional aqueous amine scrubbing of gas streams, 1940 – 1975; amine reacts with CO₂ to form the carbamate, proton transfer produces ion-counter ion product. This chemistry mandates the need for 2 amine groups to bind 1 CO₂ molecule



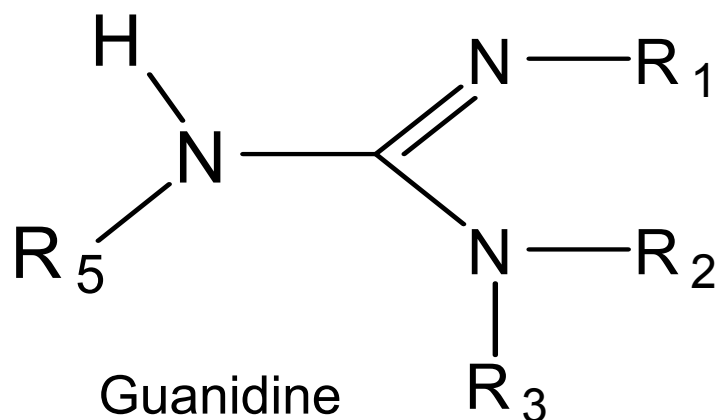
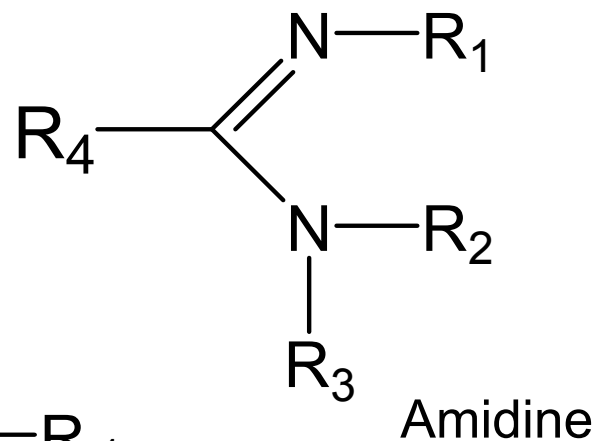
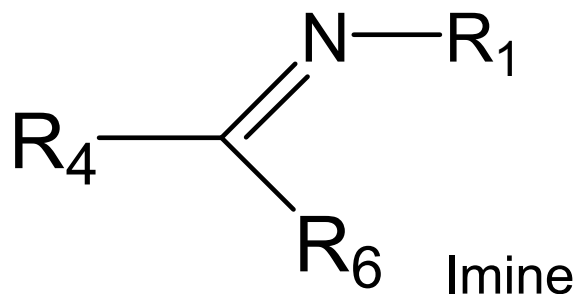
Overview and Background



G. Sartori, Exxon, early 1970's: By using a hindered amine, the initial reaction between CO_2 and the amine to form the carbamate is inhibited, allowing proton transfer to the amine to dominate.



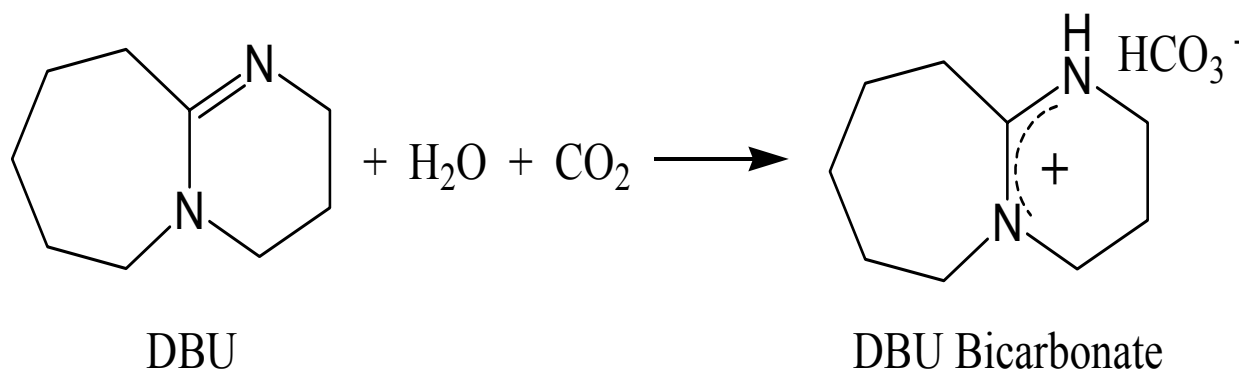
Carbon Dioxide Capture Interaction Groups



**Are strong bases that binds and interacts CO₂ reversibly
chemical reaction at 1:1 molar ratio.**



Fundamental Chemistry: Certain imino-functional compounds bind CO₂ reversible in a 1:1 fashion



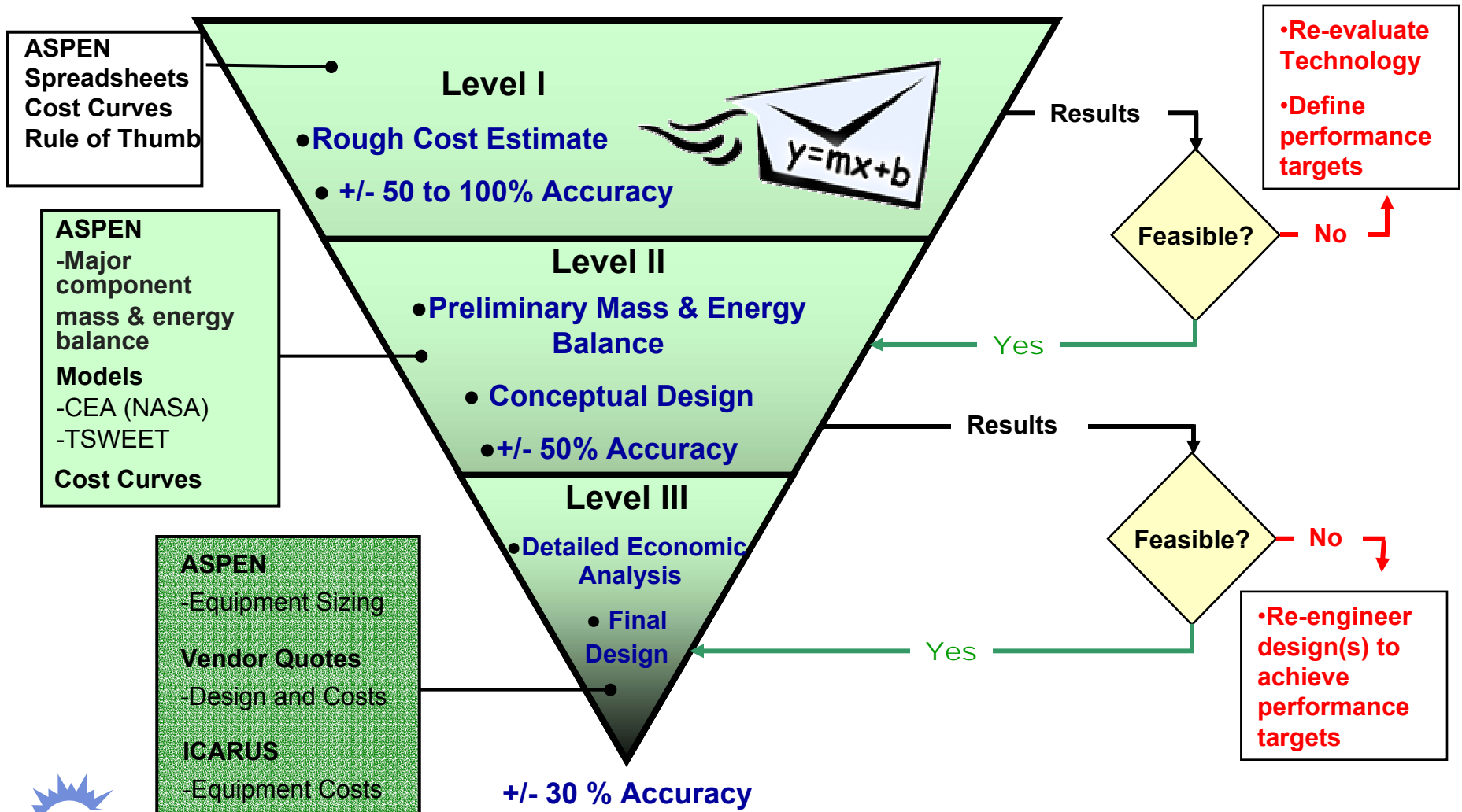
Diazabicycloundecane (DBU)

J. Org. Chem. 2005, 70, 5335-5338

Preliminary System Analysis



Systems Analysis Level of Detail



Solid Amine Adsorbent *Advantage*

Reduction in Heating Capacities and Stripping steam for CO₂ regeneration

Amine-Enriched Sorbents		
Heat Capacity (Btu/lb-°F)		0.3
ΔT Regeneration		80°F
Regeneration Energy (Btu/lb CO ₂)		
Sensible		183
Reaction	+	600*
Vaporization	+	0
Total	=	783

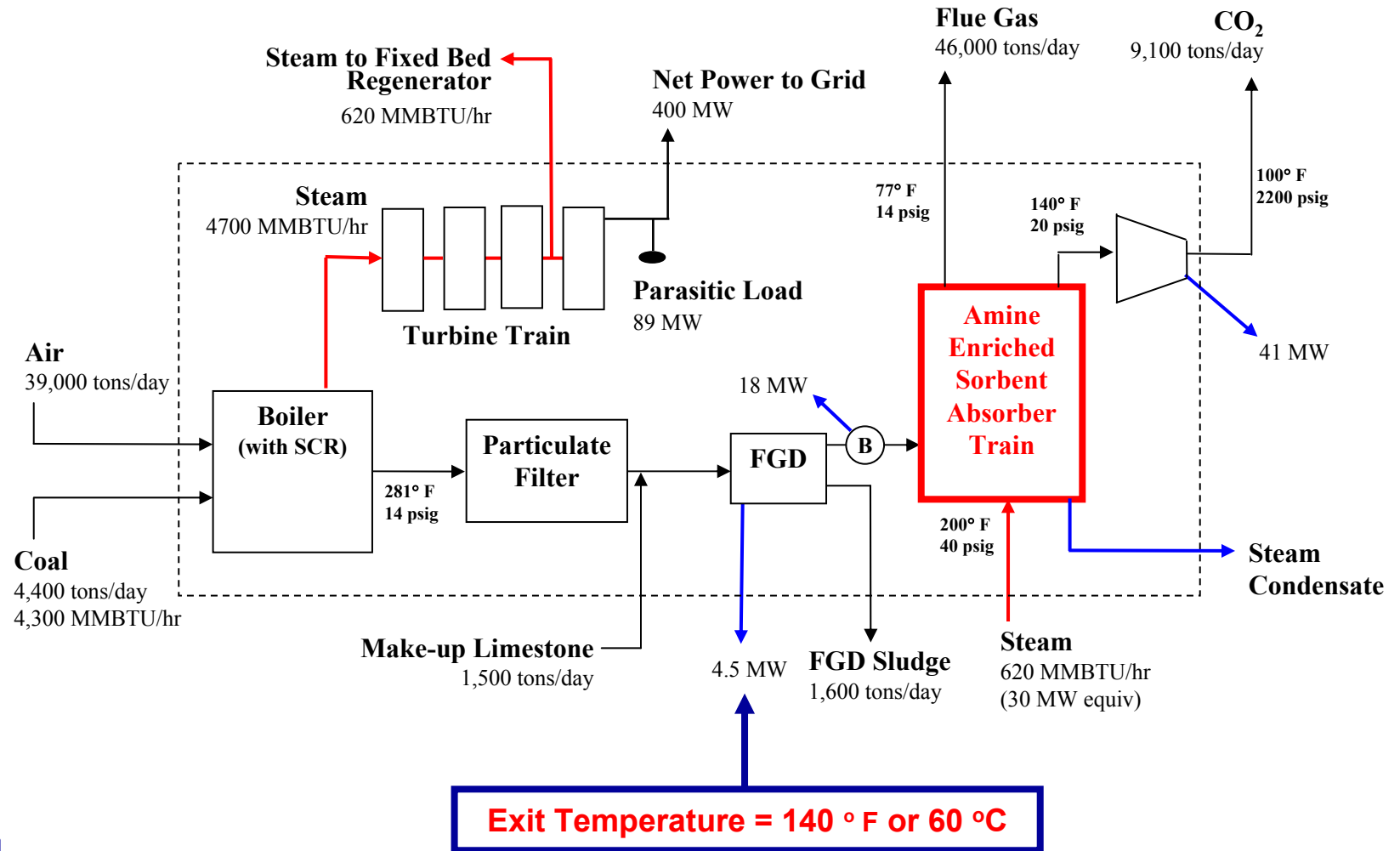
30% MEA [1]		
Heat Capacity (Btu/lb-°F)		0.9
ΔT Regeneration		105°F
Regeneration Energy (Btu/lb CO ₂)		
Sensible		941
Reaction	+	703
Vaporization	+	290
Total	=	1,934

Reference:

1. Gottlicher, G., *The Energetics of Carbon Dioxide Capture in Power Plants*, U.S. Department of Energy, National Energy Technology Laboratory, 1999



System – Post Combustion



Solid Amine Adsorbent

Advantages

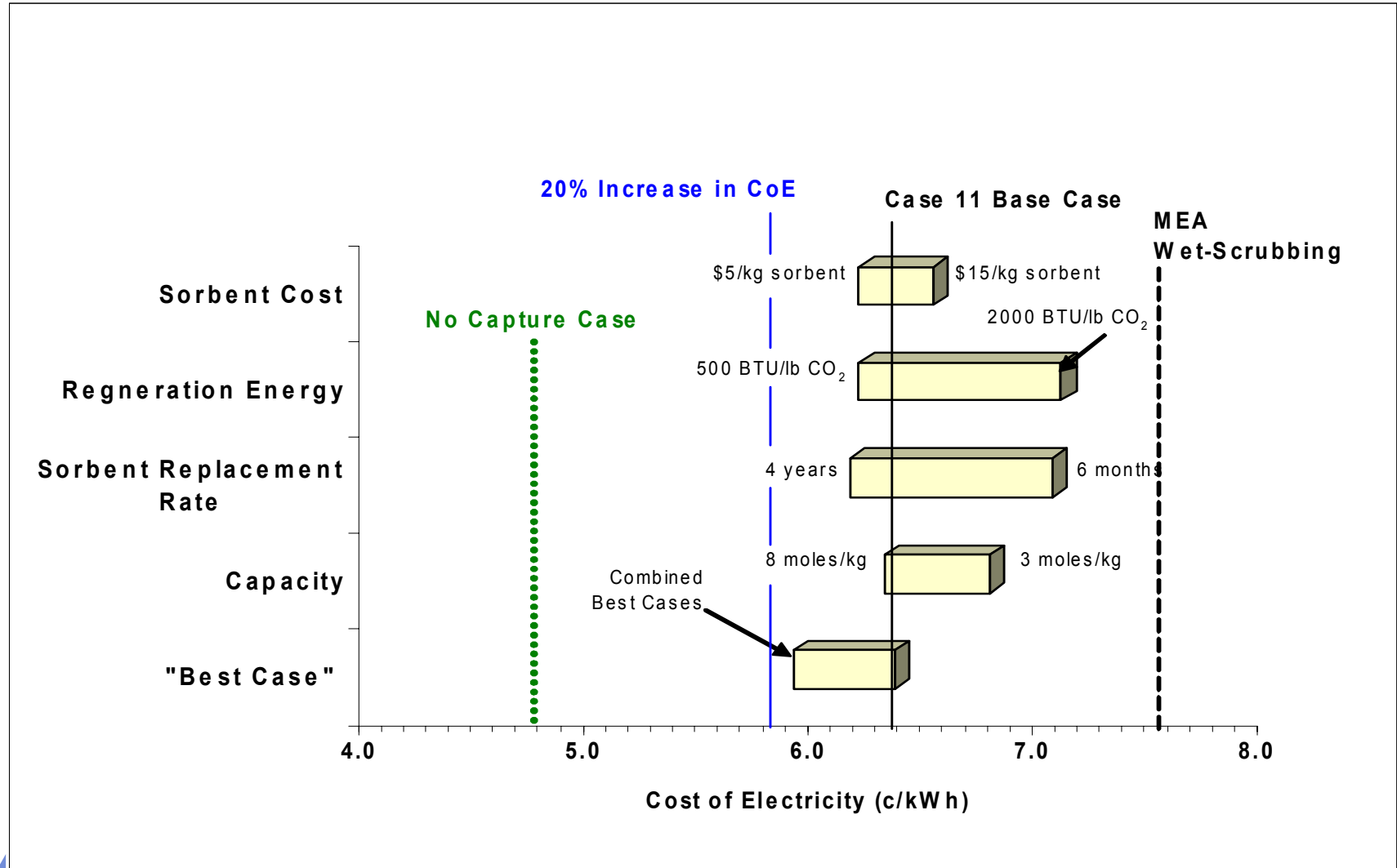
Higher CO₂ carrying capacity per lb of sorbent

	30% MEA	Amine Sorbent
Density (lb/ft ³)	22	44
Working Capacity (lb CO ₂ /lb sorbent)	0.052	0.264
Mass sorbent per pound CO ₂	19 lbs solution	3.8 lbs sorbent
Volume per Pound CO ₂ (ft ³ /lb CO ₂)	0.8	0.08

10x Reduction in volume to treat equivalent amount of CO₂



Preliminary System Analysis

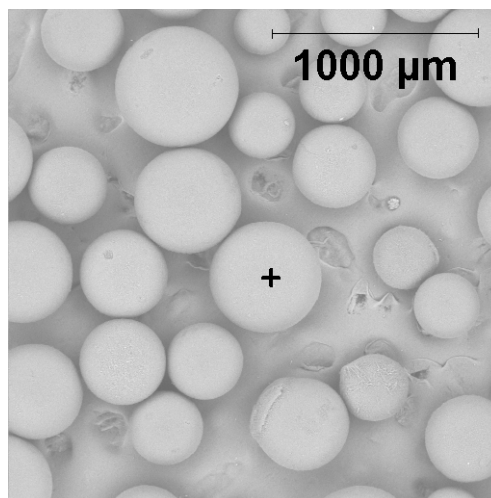


Experimental



Materials and Reagents

- **Chemicals from Aldrich Chemicals**
 - 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)
 - Methanol Reagent Grade
- **Mitsubishi Chemicals**
 - Diaion ® HP2MG Poly methyl(methylacrylate) Bead
 - PMMA



Particle size >250 μ m

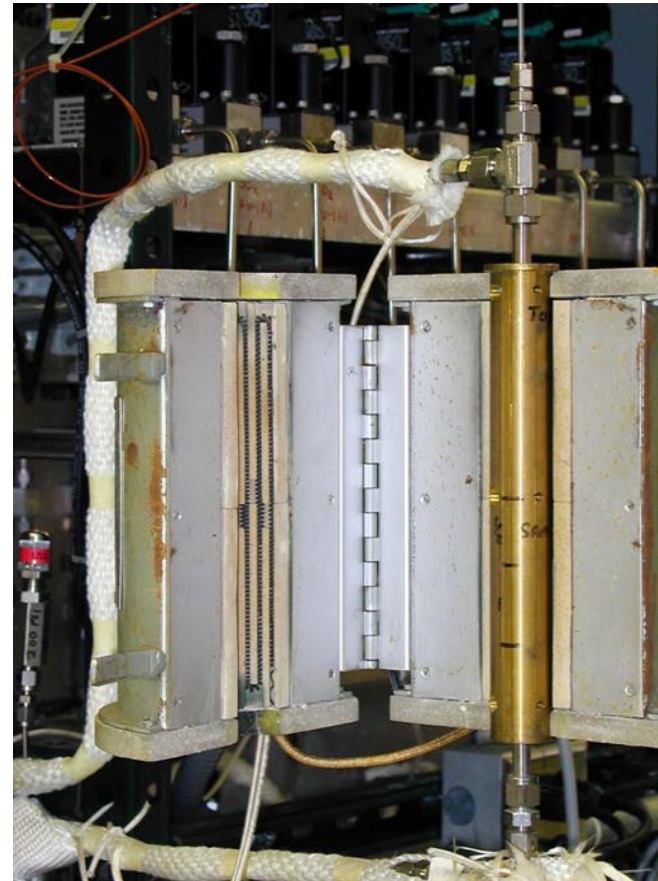
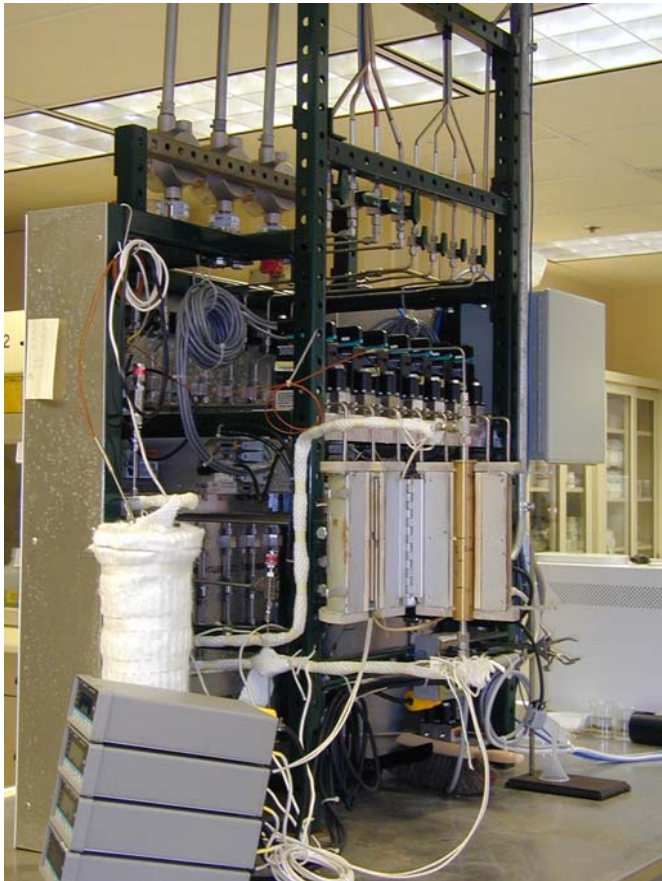
Preparation of Immobilized Adsorbents

- **75 grams of PMMA Beads placed in 300 ml of methanol and agitated**
- **Addition of the DBU at various weights ratio**
 - 7.5 grams 10 (Beads/DBU wt. ratio)
 - 15 grams 5 (Beads/DBU wt. ratio)
 - 30 grams 2.5 (Beads/DBU wt. ratio)
- **Heated over the temperature range of 25-90 °C**
- **Vacuum pressure range of 760-10 mmHg**
- **Stored in refrigerator until testing**

US Patent 5,876,488



NETL Carbon Dioxide Capture Reactor

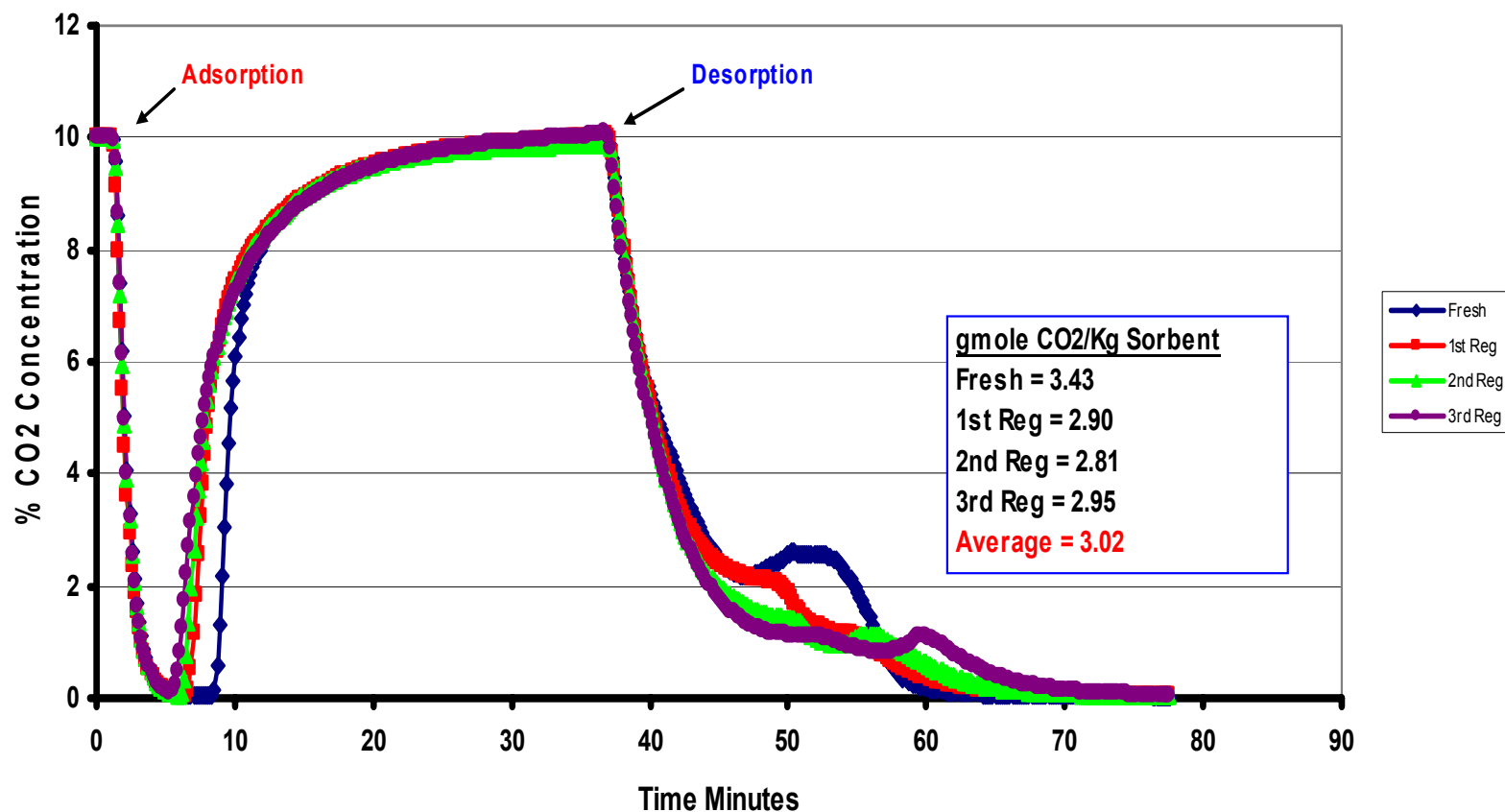


Experimental Conditions

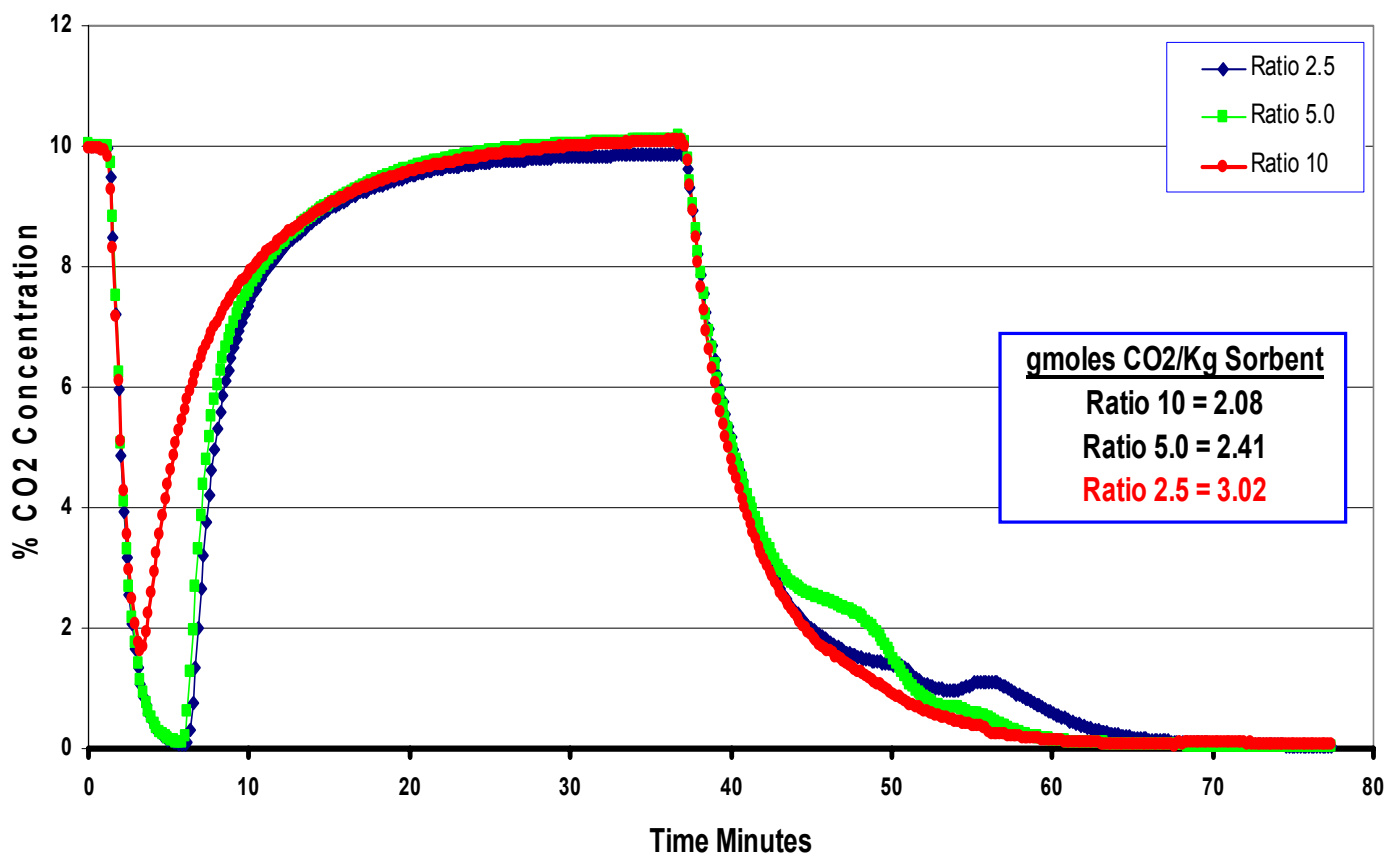
- 1.0 Gram sample (Immobilized Secondary Amine Sorbents)
- He/2% H₂O Pretreatment at 25 °C (150 ml/min)
- 10% CO₂/2 % H₂O/He at 25-65 °C (100 ml/min) **Adsorption**
- He/2% H₂O at 90 °C (150 ml/min) **Desorption**
- Pfeiffer Vacuum OminiStar 300 Mass Spectrometer



Breakthrough Curve for DBU at 2.5 Loading Weight Ratio



DBU Loading Effect on the Performance of Immobilized Adsorbents at 25 C



Performance of PMMA/DBU Immobilized Adsorbent at 25 °C

Sorbent	Wt. Ratio PMMA/DBU	Surface Area m ² /g	Pore Volume ml/gram	gmole CO ₂ / Kg sorbent
Diaion ® HP2MG ¹	NA	5.79	1.12	0.0
DBU-1	10	369	1.10	2.08
DBU-2	5	207	0.84	2.41
DBU-3	2.5	94	0.58	3.02

¹ Diaion ® HP2MG Poly methyl(methacrylate) Bead – PMMA



XPS Analysis of DBU-3 at Various Temperatures

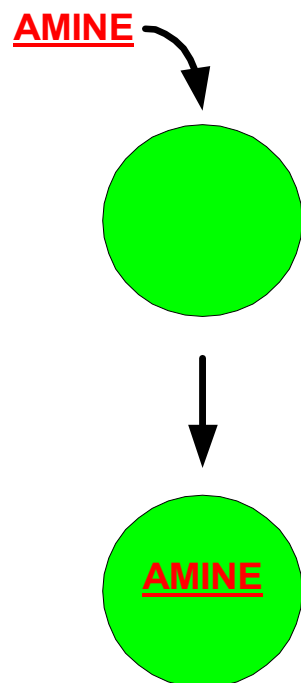
Temperature °C	gmole CO ₂ /Kg sorbent	XPS N1s
25	3.02	1.03
45	2.47	NA
65	2.34	1.26

Good Stability of the DBU within the Diaion ® HP2MG Poly methyl(methacrylate) Bead

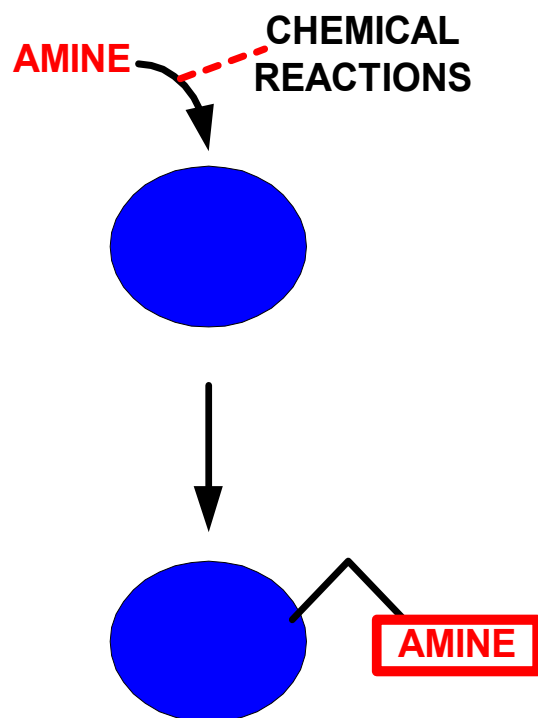


Pathways to Solid Amine Adsorbents

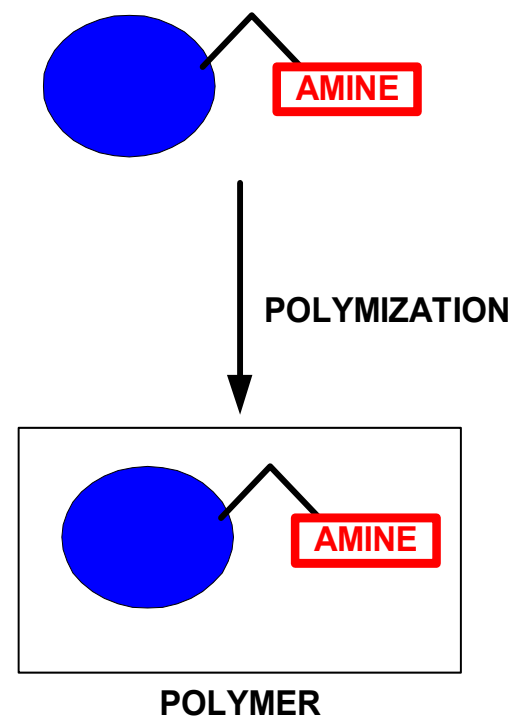
IMMOBILIZATION



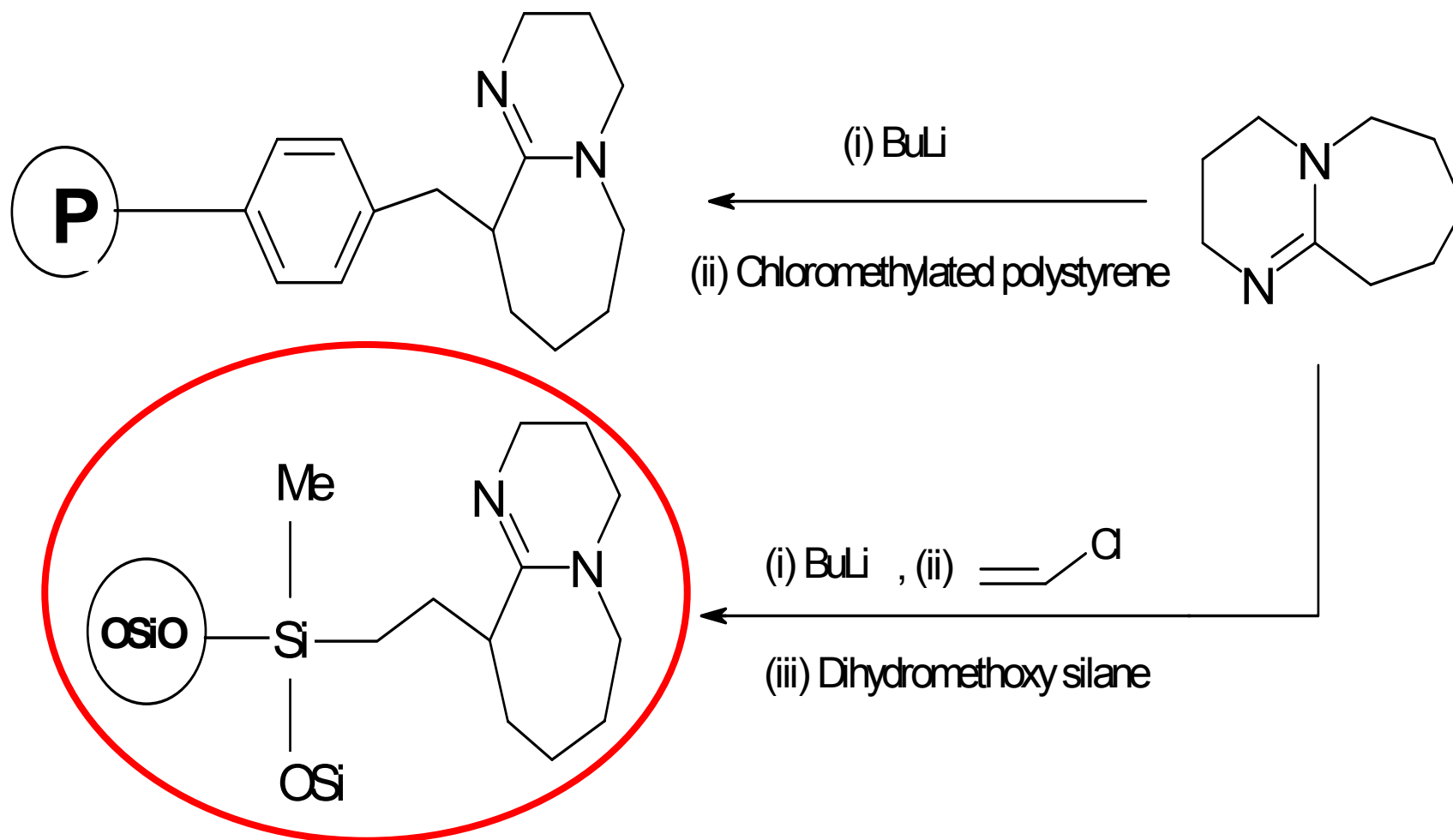
SYNTHESIS



POLYMERIZATION



Initial Proof of Concept: A DBU-functional adsorbents

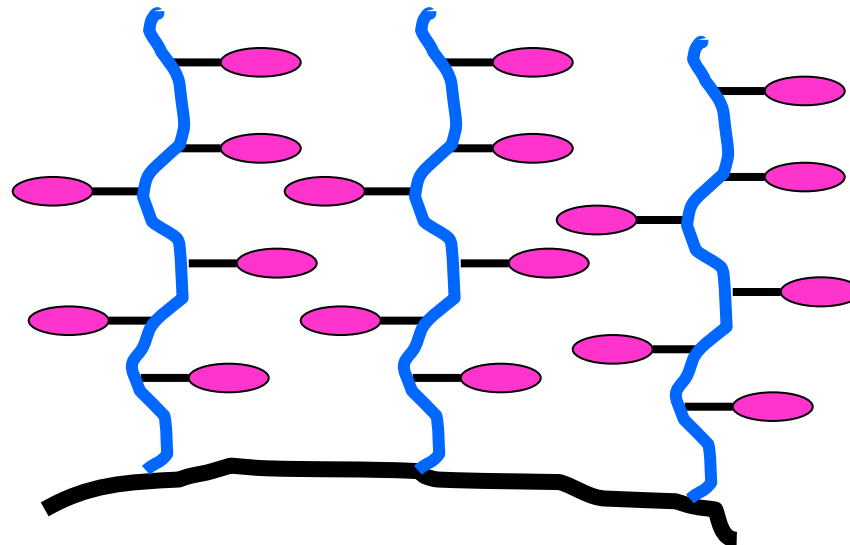
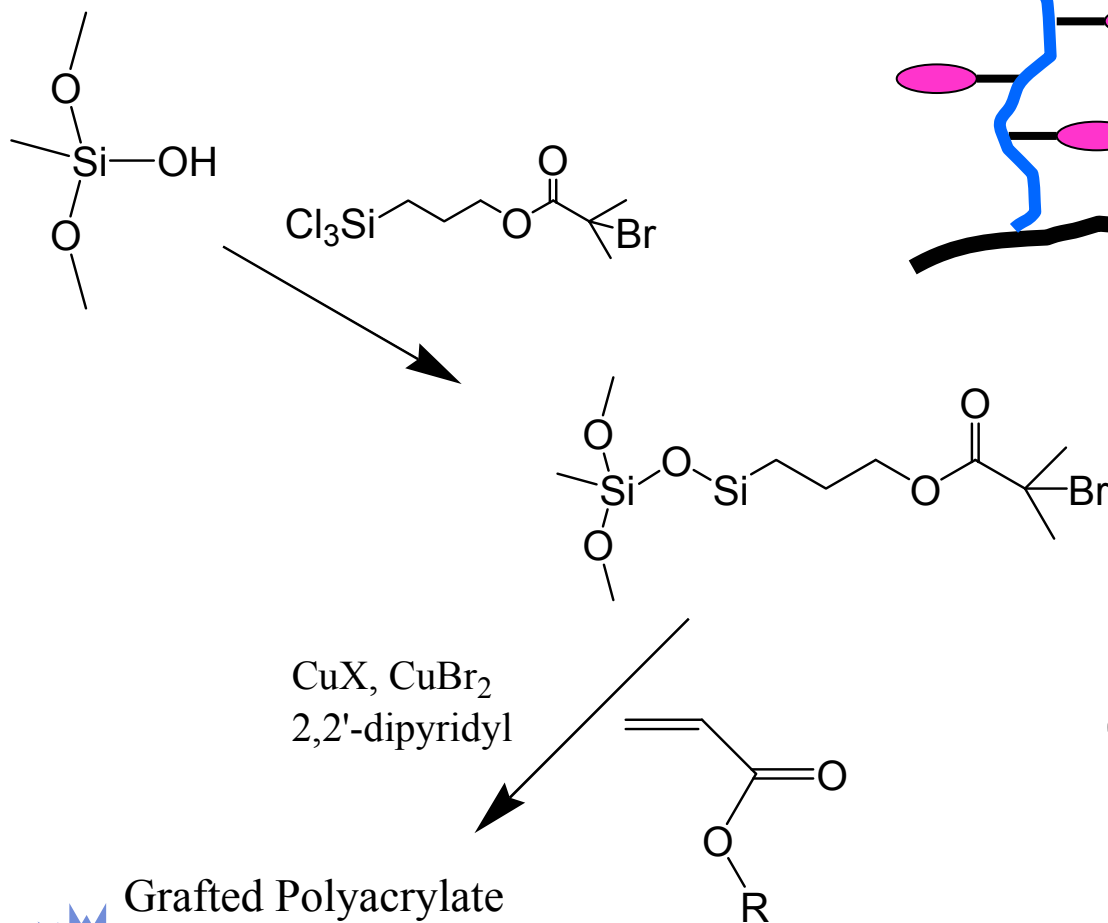


A DBU-functional silicone Adsorbent

Capture Temperature °C	gmole CO ₂ /Kg Sorbent	XPS N1s
25	3.31	4.2
45	3.26	NA
65	3.19	4.0



Polymeric DBU-acrylate



Increase Amine Loading

Polymeric Adsorbents
3-5 gmole CO₂/Kg Sorbent



Conclusions



Conclusions

- The regenerable solid Tertiary adsorbents were capable of capturing carbon dioxide in levels greater than **3 gmole CO₂/Kg adsorbent** baseline.
- Adsorbents were capable of capturing CO₂ up to 65 °C.
- Tested in substrate systems.
 - Immobilization of DBU was stable
 - Synthetic Adsorbent was more at the higher temperatures
- Currently testing monomers and polymers of the imine and other amine based adsorbents (**3-6 gmoles CO₂/Kg adsorbent**).



Acknowledgements

- **Abbie Layne** – Divisional Director of Separation and Fuels Processing Division
- **Geo Richards** – Focus Area Leader for Energy System and Dynamics



Preliminary System Conceptual Design

